

BACKGROUND OF THE INVENTION

The production of chlorine and caustic soda from sodium chloride solutions, the production of aluminium from molten salts and the electrometallurgy are nowadays the main electrochemical processes of industrial interest. In particular, chlor-alkali electrolysis is carried out according to three types of technologies, respectively the mercury cathode, the diaphragm and the membrane one. The latter type of electrolysis is the most advanced and since a few years by now represents the only alternative for building new plants in view of the lower electric energy costs and of the virtually absent environmental impact, whilst the mercury cathode and diaphragm technologies survive in already paid-off plants in which the higher variable costs are at least in part balanced by the lower investment costs. To make the operation of such plants acceptable in a situation of rising electric energy prices and of growing concern for the human health and the environment, a continuous technological improvement has been observed in the last years which in the case of diaphragm technology has led to the definition of inert fibre-based diaphragms in replacement of the originally employed asbestos, and to modifications directed to electric energy consumption reduction in the design of anodes and cathodes.

Focusing the attention on the anode design, it has been observed in particular the replacement of the so-called box-type anodes with expandable-type anodes, provided with forced expansion means optionally with controlled action.

The box-type anodes, born as a replacement of the old graphite anodes whereof they substantially maintain the external shape (see for instance US 3,591,483) consist of a titanium sheet provided with openings, for instance an expanded sheet, folded so as to form an empty box (wherefrom they are called box-type anodes), shaped as a flattened rectangular-base prism. During the electrolyzer assemblage the anodes, which are secured in a multiplicity of parallel rows on a supporting and electric current distributing base, are intercalated between corresponding rows of cathodes, also shaped as flattened boxes formed by perforated sheets or meshes of metal wire covered by a porous diaphragm

consisting, as previously mentioned, of inert fibres stabilised with a binding polymer. This operation of insertion is rather delicate and, to prevent the diaphragm from being damaged by strokes or by rubbing against the anodes, the latter have substantially lower widths than the gap between the rows of diaphragm-bearing cathodes. It follows that, during operation, the sensible gap between anodes and diaphragms entails an elevated voltage, whereto a high electric energy consumption is associated.

To overcome this drawback, particularly heavy in times of growing prices of electric energy, the expandable anodes were introduced, again shaped as a flat box, but with the two major surfaces capable of contracting, that is of getting closer or more spaced apart although remaining mutually parallel (see for instance US 3,674,676). In particular, when they are assembled in the electrolyzers, they anodes are kept in the restrained position by suitable constraints thereby assuming a reduced width which allows preventing damages to the diaphragms. Once positioned the anodes between rows of cathodes, the constraints are extracted leaving the anode surfaces free to expand under the effect of the intrinsic elasticity of the structure. The constraint extraction does not present particular difficulties since the electrolyzer is free of cover in the assembly phase of the anodes between the rows of cathodes, therefore the access to the anodes is entirely free.

Further developments of the expandable anodes are represented by the introduction of forced expansion devices, optionally provided with means for adjustment (see for instance US 5,534,122 and T MI2003A 000106), whose aim is allowing that, after the expansion of the anodes, a complete adhesion of the anode sheets to the diaphragm surfaces is obtained also in the zones lacking planarity so as to further minimise the electric energy consumption.

The box-type anodes, as well as the improved expandable types, are fixed, as said above, on a conductive supporting and current distributing base. From an electric standpoint this arrangement implies that the anodes are reciprocally connected in parallel. The corresponding electrolyzers are known as monopolar electrolyzers: in the electrolysis plants consisting of a multiplicity of electrolyzers of

this type the operation is associated to reduced overall voltages with high electric currents which must be generated by relatively expensive rectifiers. The rectifier investment is decreased if, for a given power, the generation occurs in form of relatively reduced currents and high voltages: such kinds of rectifiers require the use of electrolyzers known as bipolar electrolyzers.

The bipolar electrolyzer, for instance described in US 3,855,091, consists of an assembly of more elements of the type represented in the three-dimensional section of figure 1, wherein (1) indicates the body of the element, usually made of carbon steel provided a titanium lining (2) on the anode side, (3) the titanium sheet anodes provided with openings and with a film of catalytic material for chlorine evolution, where the sheet, which is U-folded forming a hollow internal space, is connected to the vertical wall (4) by means of support structures (5), (6) a nozzle for extracting the product chlorine and for feeding the sodium chlorine solution through a coaxial tube not shown in the figure, (7) the cathodes constituted by a series of parallel flattened boxes (known as cathode fingers) formed by a sheet provided with openings or a metal wire mesh whereon the porous diaphragm of inert fibres fixed with a perfluorinated binding polymer not shown in the figure is deposited, and (8) the anode flange which, pressed against the corresponding cathode flange (9) together with an appropriate gasket not shown in the figure, ensures the hydraulic sealing preventing the release of the reaction fluids to the external environment. Figure 2 schematically shows a top-view section of a bipolar electrolyzer structure resulting from the assemblage of elements of the type represented in figure 1, limited to three elements for the sake of simplicity: it can be noticed in particular that the anodes (3) result positioned in the hollow spaces existing between the cathodes (7) of the subsequent element and that the latter, instead of being secured to a single conductive support base as in the case of the monopolar electrolyzers, are subdivided into equal groups, each group being secured on the vertical wall of each element. Such an arrangement entails the electrolysis to be carried out, for a given installed power, with relatively reduced currents and high voltages that, as mentioned before, allows an industrial plant to make use of rectifiers characterised by lower investment costs. Since the anodes

of figures 1 and 2 have a rigid non expandable structure of substantially inferior width than the gap between two adjacent cathode fingers in order to avoid damaging the diaphragms during the assemblage, it is apparent that in the assembled electrolyzer a sensible distance exists between the relevant surfaces: this situation, which is entirely similar to the one experienced in the monopolar electrolyzers equipped with box-type anodes, entails a remarkably higher electric energy consumption for the bipolar electrolyzers equipped with rigid-type anodes than for the correspondent monopolar electrolyzers provided with expandable-type anodes.

The observation of figures 1 and 2 allows to understand that, from the moment that the elements are pressed one against the other and the electrolyzer is formed, it is not possible anymore to have access to the electrodic packages consisting of intercalated anodes and cathodes since the whole is practically sealed by flanges (8) and (9). This situation doesn't allow to use expandable anodes of the kind known for monopolar electrolyzers provided as seen with constraints that can be extracted after the assemblage. The interest for diminishing the energy consumption also in the bipolar electrolyzers has resulted in designs of expandable-type anodes, for example as claimed in Japanese Patent JP57032391, wherein the rigid anodes of figures 1 and 2 are modified as shown in figure 3 (top-view of a single anode) by operating a cut in correspondence of the curved terminal part (10) so as to permit the two surfaces (11) of the modified anode to rotate towards the outside around the points of fixing (12) to the support structure (5), as indicated by the arrows. In this way, the gap between the facing surfaces of the diaphragms and the anodes is sensibly reduced or even suppressed by suitably adjusting the elasticity of the anode structure. The possibility of damaging the diaphragms and/or the anodes and cathodes while drawing one element near the other is overcome in an equivalent fashion to what is known for the monopolar electrolyzers, that is relying on the use of constraints (13) capable to maintain the anodes in a restrained position (figure 4, top-view of a single anode): the problem of accessing the anodes after the assemblage precluding any possible manual intervention on the elements is circumvented by

making the constraints (13) out of a material which is soluble in the chlorine-containing sodium chloride anolyte, for instance using steel or copper or nickel wires as constraints: in this way, after a short period of operation, around a few hours at most, the constraints (13) are self-destroyed thus releasing the surfaces (11) which may now freely rotate around the points (12) thereby approaching or contacting the diaphragm surfaces. By operating with these measures it is possible to decrease the operating voltage of each single element, at a current density of 2000 A/m², from about 3.6 Volt, typical of the rigid anode-equipped elements, to 3.4 Volt.

The disclosed measure is effective in the electrolyzer assembly phase, but introduces the problem of possible damaging in the phase of disassembly for maintenance, when pulling one element apart from the other may determine a friction of the anode surfaces against the diaphragm and cathode surfaces, with strong chances of tearing or warping the sheets (11).

DESCRIPTION OF THE INVENTION

The scope of the present invention is to provide an expandable anode structure suitable for bipolar electrolyzers allowing both the assembly and the disassembly of elements with no damaging hazard, while continuing to ensure the effective approaching and optionally the contact between the surfaces of the anodes and of the cathode finger-deposited diaphragms.

According to a first aspect, the present invention describes a reversible-type expansion device housed in the hollow internal space of the anodes capable of forcing the anode surfaces in a spread out position during the assembly phase of the elements of an electrolyzer with reduction or even suppression of the gap between the facing surfaces of the anodes and of the cathode finger-supported diaphragms and in a restrained position of such surfaces during the phases of disassembly for maintenance.

In a second aspect the device of the invention is characterised by the possibility of presetting the extent of the anode span during the assembly phase of the

elements.

According to a third aspect the expansion device of the invention owes its reversibility to a component provided with elasticity, housed in the hollow internal space defined by the opposed surfaces of each anode and fixed thereto, and connected to a further mobile component capable of reversibly shifting inwards or outwards said space respectively during the assembly and the disassembly of the elements of an electrolyzer simultaneously provoking the expansion or the contraction of the anode surfaces.

According to a fourth aspect the mobile component of the expansion device consists of a variable section pivot provided with a tip section of electrically insulating material, in contact with the diaphragm surface during the assembly and disassembly operations, wherein said pivot comprises an elastically responding portion placed on the section opposite the tip section of insulating material.

According to a fifth aspect the major and minor diameter sections of the variable section pivot of the expansion device determine respectively the contraction and the expansion of the surfaces of each anode.

According to a sixth aspect the electrically insulating material of the tip section of the pivot of the expansion device consists of polytetrafluoroethylene or other polymer resisting to the aggressive action of chlorine and the portion having elastic behaviour is a spring which is respectively compressed or released during the phases of assembly and disassembly of the elements of an electrolyzer.

In the forthcoming part of the text and of the relative drawings the invention is explained in more detail, in particular through the description of preferred embodiments.

The present invention is directed to overcome the main limitation of the expandable anodes for bipolar electrolyzers of the prior art, wherein said limitation substantially consists of the lack of reversibility, this meaning that the anodes spread out during the assembly phase, reducing or even suppressing the gap between the surfaces thereof and those of the opposed cathode finger-supported diaphragms, but have no possibility of contracting again when, for maintenance purposes, the elements of an electrolyzer have to be disassembled. It is apparent

that, the moment an element is pulled apart from the other, the fact that the anodes are irreversibly in a spread out state entails the rubbing of the same anodes against the diaphragm and the relevant cathode finger surfaces with high damaging and warping hazards when the inevitable surface irregularities block one another. It is also clear that, moreover, the prior art method, based on the use of labile constraints, which are dissolved during the first hours of operation by the chlorine-containing sodium chloride solution in co-operation with the action of the anodic potential, and on the expansion induced by the elasticity characteristic of the anode surfaces does not allow to preset the expansion extent. It follows that, to prevent diaphragm damaging caused by an excessive pressure exerted by the anode surfaces, the same anodes are constructed imparting a moderate degree of elasticity to the surfaces thereof permitting a cautious expansion which allows to decrease the gap from the diaphragm surfaces, but not to suppress it altogether in view of the mentioned hazards.

The present invention overcomes these limitations making use of a reversible expansion device capable of provoking the gradual spreading of the opposed expandable anode surfaces of bipolar diaphragm electrolyzers during the phase of approaching one element to the other and conversely the progressive contraction during the phase of withdrawal of an element from the other as occurs during the disassembly effected to proceed with maintenance. Moreover, before proceeding with the assemblage, the reversible expansion device of the invention may be subjected to an adjustment allowing to preset the maximum degree of expansion of the anode surfaces during the assembly and thereby the distance of maximum proximity of the anode surfaces to the diaphragm surfaces. The maximum proximity of the surfaces is substantially a function of the quality of construction of the elements and of the preservation degree thereof: if the construction was effected according to rigid mechanical tolerance standards the device of the invention is adjusted so as to minimise and even suppress the anode to diaphragm surface gap, thereby allowing to get the maximum benefit during operation in form of particularly reduced electrical energy consumption. In case the construction was carried out with less rigid quality standards or if the elements

during their operative life suffered mechanical damages during the displacement associated to the disassemblies for periodical maintenance, then the device of the invention allows effecting a regulation which reduces the maximum expansion of the anodes once intercalated to the cathode fingers. In this case the distance between anode and diaphragm surfaces is higher than in the optimal situation seen above: as a consequence, a relatively higher electric energy consumption is accepted, counterbalanced however by the absence of diaphragm damaging also in the presence of elements characterised by strong geometric irregularities.

This set of advantages may be obtained in several ways: in the following, reference will be made to two particularly preferred embodiments, without this having to be considered as a limitation of the invention whereof those skilled in the art will certainly be able to identify further constructive embodiments.

The basic principle of the invention derives from the consideration that during the phase of element assembly to form an electrolyzer the only source of motion that can be exploited to obtain the expansion of the anode surfaces is given by the approaching of the elements themselves. With this principle in mind, the inventors have devised several embodiments among which two particularly preferred ones are shown in the following figures.

DESCRIPTION OF THE DRAWINGS

In addition to the figures illustrating prior art devices, as previously described making reference to the figures and precisely:

Figure 1 showing an electrolyzer of the prior art.

Figure 2 showing a top-view section of a bipolar electrolyzer of the prior art

Figure 3 showing a top view of an anode of the prior art

Figure 4 showing another top view of an anode of the prior art

the invention will now be described making reference to the following figures, wherein:

Fig. 5A is a top view of the electrolyzer of the invention with the anodes in the restrained position.

Fig. 5B is a top view of the electrolyzer of fig. 5A with the anodes in the expanded position.

Fig. 6 is a top view of the electrolyzer of fig. 5A with the anodes provided with slits.

Fig. 7A and 7B are three-dimensional representations of a top-view of the device of the invention.

Fig. 8 shows another embodiment of the invention.

DETAILED DESCRIPTION OF THE INVENTION

Figure 5A proposes a sketch of a top-view section of two electrolyzer elements in the approaching phase, wherein (1), (3), (7) and (11) indicate as in the previous figures the steel element structure, the anodes, the cathodes and the opposed surfaces of each anode consisting of a sheet provided with openings and of a catalytic coating for chlorine evolution. (14) identifies the reversible expansion device of the invention housed in the hollow internal space of each anode. The device comprises a titanium thin sheet (15) folded so as to form a rectangle with the extremities (16) partially constrained by the pivot (17) and capable of reversibly shifting outwards and inwards. The faces of the thin sheet are secured to the surfaces (11) of the anodes (3), for instance, but not exclusively, by welding points. The anode surfaces can rotate around the points of fixing to the support structures (not represented in the figure) since their extremities (26) are by no means constrained. The thin sheet (15) is provided with elasticity that can displace the extremities (16) with consequent separation or contraction of the anode surfaces (11): the extremities (16) are maintained in the restrained position of figure 5A when the pivot (17) crosses the same with the major diameter section (18) and are brought in the expanded position of figure 5B when the pivot cross them with the lower diameter section (19). To consent this movement the extremities (16) are provided with slits (25) as shown in figure 6. The pivot (17) is provided with a further tip section (20) consisting either of a cylinder of electrically insulating material or of a titanium cylinder coated with an electrically insulating material, for instance a polymer material characterised by high chemical inertia,

more particularly polytetrafluoroethylene. Between the pivot (17) and the bottom side of (15) a spring (21) whose functional role will be described in the following, is inserted. The pivot (17) crosses the spring (21) and extends beyond the bottom side of (15) in form of threaded rod whereto a nut (22) is threaded, acting as a stopper, in other words fixing the position of the pivot (17) before the start of the assembly procedures. The tip section (20) of the pivot (17) can slide along the axis of the pivot (17), for example by rotation around a thread (not shown in the figures) obtained on the terminal part of section (19). The longitudinal displacement of (20) allows adjusting the distance between the apex of the tip section (20) and the spring (21) and represents an easy way to preset the expansion extent of the device (14) and thus of the surfaces (11) of the anodes (3) prior to the assembly: in fact the expansion extent depends on the relative position of the extremities (16) provided with slits and of the different diameter sections of the pivot (17). In particular, once completed the assembly, the extremities (16) provided with slits may coincide with the major diameter section (18) (surfaces (11) restrained) or with the minor diameter section (19) (surfaces (11) in the maximum expansion position) or with the conical junction between the two sections (18) and (19) (surfaces (11) in an intermediate position). The device finally comprises a cylindrical sheath (23) whose task is to ensure the centring of the pivot (17).

The structure of the reversible expansion device of the invention is shown in figure 6 as three-dimensional representation of a top-view, wherein the various component parts are again indicated with the same reference numerals used in the previous figures.

The functioning of the device of the invention will be now described making reference to the schematic figures 5A and 5B: in the initial phase of element approaching (figure 5A) the springs (21) are extended and maintain the pivots (17) in a position with the tip section (20) protruding with respect to the extremities (26) of the surfaces (11): in particular in this position the pivots (17) cross the extremities (16) of the elastic thin sheets (15) with the major diameter section and therefore, thanks to the partially constraining action of the slits (25), the thin sheets and thus also the surfaces (11) fixed thereto are maintained in a restrained

position. In this phase, the planar cathode surfaces (24) provided with the diaphragm (27) are still at a certain distance from the tips (20). As the approaching of the elements goes on, the planar surfaces (24) come in contact with the tips (20) of the pivots (17) which are progressively displaced toward the internal hollow space of the anodes (3) compressing the springs (21): in the final phase, in which the elements are pressed one against the other (figure 5B), the pivots (17) cross the extremities (16) of the elastic thin sheets (15) with the minor diameter section or with the portion of conical junction between the two sections of different diameter. The clearance thus created with the slits (25) allow the thin sheets and the surfaces (11) of the anodes (3) secured thereto to unfold under the elastic push of the material of the thin sheets themselves and optionally of the surfaces (11). In this way the surfaces (11) come at a more or less reduced distance or even in contact with the cathode fingers (7) depending on how the position of the tip section (20) has been adjusted.

During a subsequent disassembly phase due to maintenance needs the functioning of the device is reversed: in particular, with the separation of the elements the push exerted by the cathode planar surfaces (24) on the tips (20) of the pivots (17) ceases, and the springs (21), compressed during the previous operation, stretch out pushing the pivots (17) back to the original position seen at the beginning of the assemblage, with the tip section (20) protruding from the extremity (26) of the surfaces (11). In this position the pivots (17) cross the extremities (16) of the surfaces (11) with the major diameter section and thanks to the co-operation of the slits (25) force the thin sheets (15), and thus the surfaces (11) secured thereto, in a restrained position (already seen in figure 5A) which greatly facilitates the disassembly operation preventing damages of mechanical origin, such as tears and deformations. The functioning of the device of the invention is therefore fully reversible as regards the passage from restrained position to unfolded position and viceversa, furthermore allowing, by means of a simple preset operation, to fix the distance between the surfaces (11) of the anodes (3) and the surfaces of the cathode fingers to carry out the electrolysis therewith.

The functioning of the device of the invention, discussed on the basis of the schematic figures 5A and 5B, is shown for a better understanding as three-dimensional representation of a top-view in figures 7A (assembly phase, with the pivots (17) crossing the extremities (16) with the major diameter section keeping the thin sheets (15) and the surfaces (11) of the anodes (3) in a restrained position) and 7B (assembly completed, operation phase with the pivots (17) crossing the extremities (16) with the minor diameter section allowing the maximum expansion of the thin sheets (15) and of the surfaces (11) of the anodes (3)).

A further possible embodiment of the invention is schematised in figure 8. The anode (3), whose surfaces are by no means constrained in correspondence of the extremities (26), is provided with a central pivot (28) consisting of a titanium strip fixed in (29) to the support structure (5): the titanium strip is zigzag-folded so as to form a section endowed with elasticity consisting of a serpentine (30) and is provided in correspondence of the extremity opposed to (29) with a wedge-shaped component (31), for instance obtained by folding the strip itself and securing an adequate additional sheet (32) with a welding point (33). The wedge-shaped component (31) has an acute angle apex (35) pointing towards the strip (28) and is electrically insulated at least in its planar part (34) opposed to said apex. The anode (3) may be provided with internal centring details of the device (28) not shown. The functioning of the device (28) of figure 8 is similar to that previously described for the device of figures 5, 6 and 7. In particular, during the approaching of the elements in the assembly phase the cathode planar surfaces (24), once come in contact with the planar part (34) of the wedge-shaped component (31), exert a progressive pressure on the serpentine-shaped part (30) of stripe. The contraction of the serpentine (30) allows the progression of the component (31) between the extremities (26) of the surfaces (11) of the anodes (3) determining the progressive expansion and approaching thereof to the surface of the cathode finger (7) - deposited diaphragms. The adjustment of the expansion of the surfaces (11) of the anodes (3) is in this case obtained by suitably changing the acute angle (35) of penetration of the wedge-shaped component (31) between the

extremities (26) of the surfaces (11). In the disassembly phase the functioning of the device is reversed: in fact with the separation of the elements the push of the planar surfaces (24) on the component (31) and therefore on the serpentine (30) ceases, and the latter may thus progressively stretch out. The extension of the serpentine (30) in its turn determines the outwards sliding of the component (31) and eventually the contraction of the anodes (3) due to the progressive closing of the surfaces (11). Thus also the device of figure 8 is characterised by those features of reversibility which, as previously said more than once, are necessary to permit the assembly and disassembly of elements of a diaphragm bipolar electrolyzer without incurring serious mechanical damage. Moreover also the device of figure 8 is provided with the possibility of presetting the expansion of the surfaces (11) of the anodes (3).

The above description shall not be understood as limiting the invention, which may be practiced according to further different embodiments without departing from the scopes thereof, and whose extent is univocally defined by the appended claims.